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Investigation of Products of Tire Wear

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NATIONAL BUREAU OF STANDARDS REPORT

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INVESTIGATION OF PRODUCTS OF TIRE WEAR

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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INVESTIGATION OF PRODUCTS OF TIRE WEAR

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U.S. DEPARTMENT OF COMMERCE
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ABSTRACT----------0

A. INTRODUCTION----------1

B. TRAFFIC SIMULATOR----------3

1. General Description----------3
2. Test Pavements----------6
3. Test Conditions and Procedures----------10

C. SAMPLE COLLECTION AND ANALYSIS PROCEDURES----------11

1. Particulate Collection Procedures----------11
2. Volatile Collection and Analysis Procedures--------18
3. Particulate Analysis----------21
4. Tent Leakage Tests----------29

D. RESULTS AND CONCLUSIONS----------30

1. Particulate----------30
2. Volatiles----------33
3. Application to Road Conditions----------35

E. COMMENTS AND SUGGESTIONS----------35

F. CONTRIBUTING PERSONNEL----------38

TABLES

I. PORTLAND CEMENT CONCRETE SURFACES AGGREGATE SIEVE ANALYSES----------8

II. PORTLAND CEMENT CONCRETE COMPRESSIVE STRENGTH----------9

III. SUMMARY OF TRAFFIC SIMULATION OPERATION----------12 -14

IV. SUMMARY OF ANDERSON SAMPLER DATA----------15

V. HI-VOL FILTERS----------17

VI. ANALYTICAL DATA----------20

VII. RESULTS OF THE ANALYSIS OF THE TWELVE COLLECTED SAMPLES----------24

VIII. EXTRACTION DATA----------27

IX. LEAKAGE TEST DATA----------31

INVESTIGATION OF PRODUCTS OF TIRE WEAR

Abstract

A limited preliminary study was undertaken of the emission of products of wear from automobile tires. The compromise experiment used real tires at typical loads, real pavements, speeds, and ambient conditions. Volatile and particulate samples were collected and analyzed. Results and suggestions concerning future studies are provided.

A. INTRODUCTION

The National Bureau of Standards undertook a limited study of the emission of products of wear from automobile tires with major support from the Mobile Source Pollution Control Program of the Environmental Protection Agency (EPA). The major interest was to provide better information concerning the composition of tire wear emissions into the air. In brief, the approach was to operate several tires in a controlled atmosphere and to analyze volatile and particulate samples collected while the tires were running.

The project used the traffic simulator facility of the American Oil Company, Research and Development Department at Whiting, Indiana, for the tire emission studies. The general procedures and methods used were developed cooperatively by NBS, EPA, and AMOCO staff. The analysis of volatile emissions was conducted by AMOCO, while the particulate analysis was handled by NBS. The experimental operation in Whiting was conducted under the general observation of an NBS staff member who, in consultation with other NBS and EPA staff, was responsible for the determination of the specific tests and order of operation of the traffic simulator and the volatile analyses.

Several hundred thousand tons of rubber are estimated to be worn annually from vehicle tires in the United States.[1,2] This amounts to 4.3 tons (7800 kg) daily per million population, with each automobile generating 0.2 to 0.4 g/mi (0.1 to 0.25 g/km) of tire wear products (in this test our wear rate was about 0.1 g/mi (0.06 g/km) per tire).

Many studies have been made concerning vehicle tire wear. However, almost without exception they have been concerned with improvements in performance, reducing costs, etc. Very few studies have been made on the form or composition of tire wear emissions. There have been indications of carcinogenic polycyclic aromatic hydrocarbons in some tires.[3,4]

Major problems in studying tire emissions are: distinguishing the small quantity of tire wear products from the earth, pavement, and other material in samples collected from normal tire use; simulating normal tire wear under laboratory conditions; and identification of the rubber and many of its decomposition products. Lagerwerff[5] has analyzed earth samples near a highway using zinc as the rubber tracer. This can be a convenient way to follow the rubber particulates, as tires often have as much as 1% zinc oxide in them.

This project represents a preliminary look at the tire wear problem from the point of view of air pollution. The experimental plan represents a compromise between the ideal of collecting the tire emissions under very realistic driving conditions, and the ideal of collecting a very clean sample (both particulate and volatile) without the presence of complicating foreign material. The realization of the first ideal requires an on-the-highway test while the second requires controlled laboratory tests. In our compromise the test uses real tires at typical loads, real pavements, speeds and ambient conditions. However, to collect an uncontaminated sample and to achieve a mass balance, an enclosed volume is necessary.

Because of this the tires must be run in a small circle. To achieve a better balance between realistic driving conditions and uncontaminated sample would require a much greater investment of time and equipment than was justified for this preliminary investigation.

B. TRAFFIC SIMULATOR

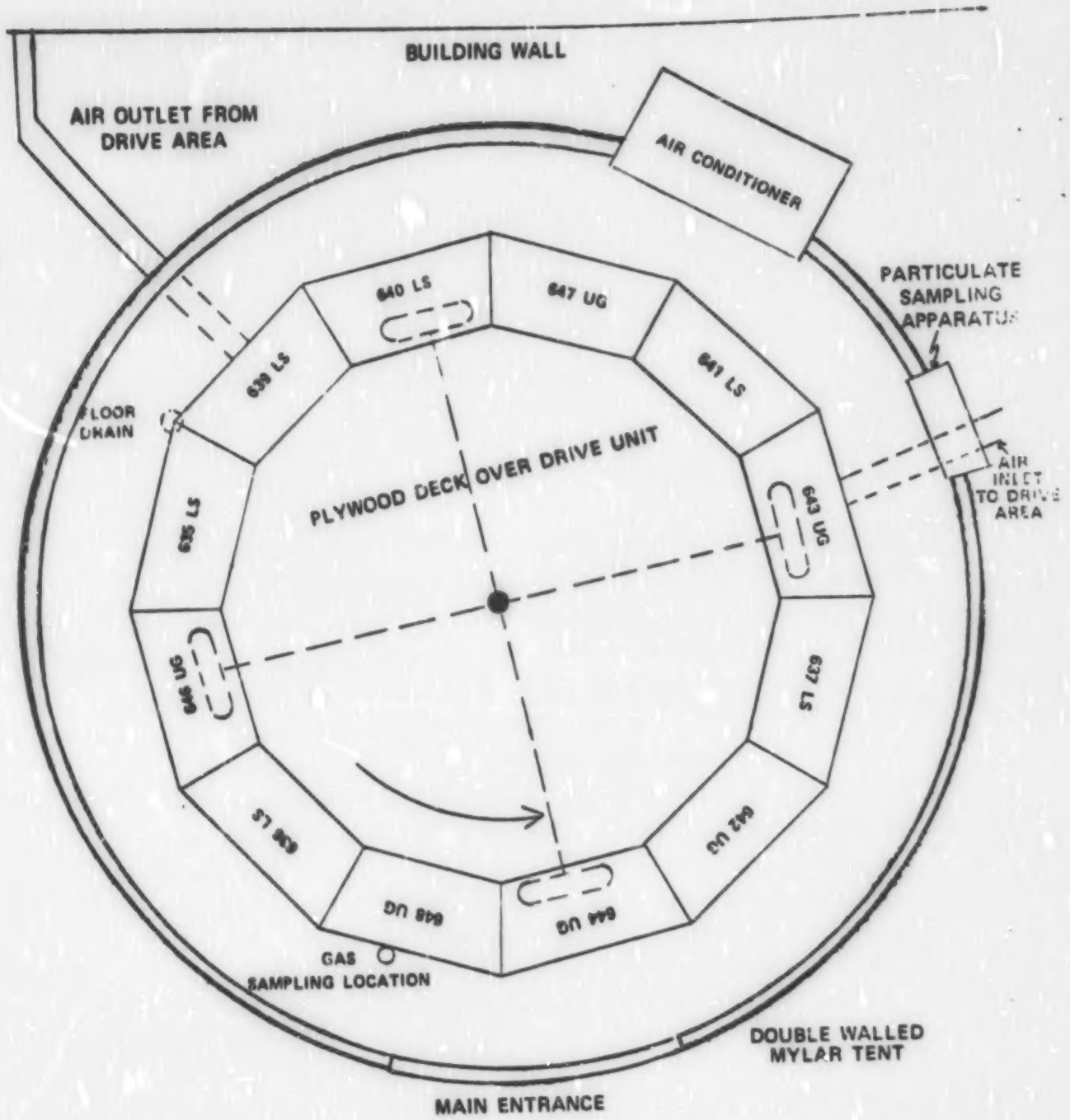
1. General Description

The American Oil Company traffic simulator consists of a turntable of 4-meter diameter supported by a central column (Figures 1, 2, and 3). The turntable includes four steel arms each with a wheel and tire mounted at the end of a pair of loading pantographs. The tires ride over twelve test pavement segments arranged to form a continuous circular track. A double-walled mylar tent encloses the track and turntable. A closed-loop air conditioning system controls the temperature in the facility.

A hydraulic system on each axle continuously varies the axle length over a 4.5 cm range as the turntable revolves. The hydraulic systems for the four axles are interlocked and centrally controlled by a master valve so that all four wheels move in or out simultaneously (each in-out cycle is a "stroke"). The radius of the arms (center line of machine to tire center line at mid stroke) is 197 cm.

FIGURE 1

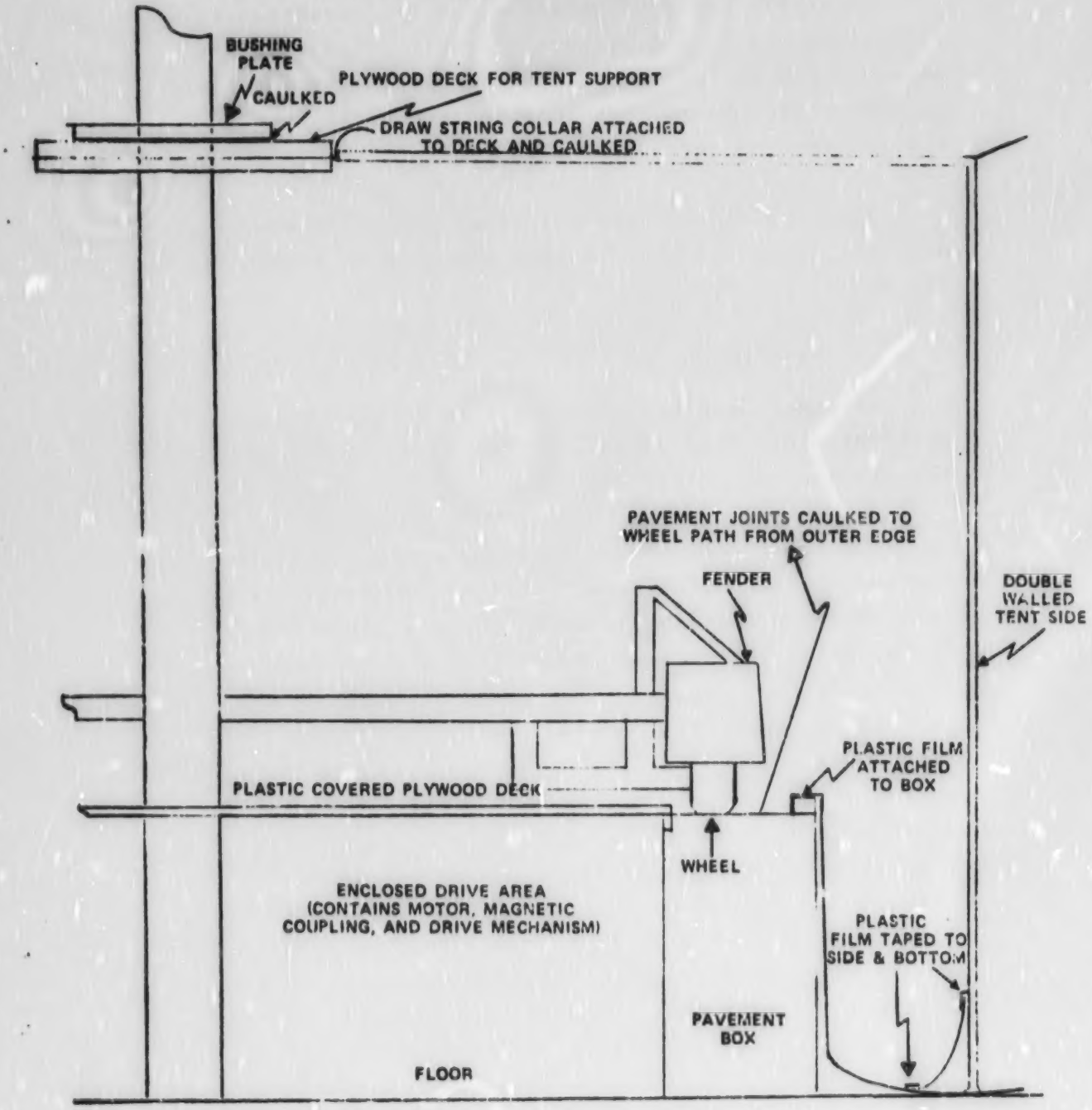
TRAFFIC SIMULATOR FLOOR PLAN



LS—CRUSHED LIMESTONE
UG—UNCRUSHED GRAVEL

FIGURE 2

TYPICAL SECTION OF TRAFFIC SIMULATOR


BUSHING PLATE
CAULKED
PLYWOOD DECK FOR TENT SUPPORT
DRAW STRING COLLAR ATTACHED TO DECK AND CAULKED
PAVEMENT JOINTS CAULKED TO WHEEL PATH FROM OUTER EDGE
FENDER
DOUBLE WALLED TENT SIDE
PLASTIC FILM ATTACHED TO BOX
PLASTIC COVERED PLYWOOD DECK
WHEEL
ENCLOSED DRIVE AREA (CONTAINS MOTOR, MAGNETIC COUPLING, AND DRIVE MECHANISM)
PLASTIC FILM TAPED TO SIDE & BOTTOM
PAVEMENT BOX
FLOOR

Turntable speed-of-rotation, ambient temperature, wheel-pass count, and various critical potentials and currents for the drive and control systems are displayed on the control board. The temperature within the traffic tent is recorded continuously.

Each individual pavement segment has adjustable supports, permitting the entire track to be brought to the same level.

2. Test Pavements

All test pavement segments were constructed using regular AMOCO pavement containers (boxes) and typical concrete finishing equipment.

The traffic simulator is primarily a pavement-testing machine. For example, it has been used to measure the effects of studded tires on pavements. The pavement segments are therefore designed to simulate a real highway. The pavement boxes were fabricated of welded 1/4 inch (6.4 mm) steel sheets with added stiffening. Individual pavement sections were 61 cm wide, 130 cm long on the outer side and 97 cm long on the inside. They were supported by brackets and threaded leveling rods along their inner and outer sides. The leveling rods provided the adjustment necessary to provide a level wheel path in the test track. The pavements were poured in two parts; a concrete base which filled most of the box and a surface layer having the desired aggregate.

64

The bases for the test pavements consisted of a single layer of 3000 psi air-entrained ready mix concrete. Prior to pouring the bases, the insides of the metal boxes were precoated with a special parting material to allow removal of the bases after use of the test pavements. After pouring, the base was cured a minimum of thirteen days (three days moist under plastic initially) prior to placement of the surface layer.

All pavement surfaces were four inches thick and representative of air-entrained concretes used routinely by the Indiana and Illinois Highway Departments. One-half of the surfaces contained crushed limestone aggregate and one-half contained uncrushed gravel aggregate. The surface concretes were obtained locally (Whiting, Indiana) from a ready-mix concrete supplier. Sieve analyses of the aggregates are shown in Table I. Compressive strengths of the Portland Cement concrete are shown in Table II. A vibrator was used to level and compact the plastic concrete. Minor surface roughness was "dressed up" with a wood float. The final surface finish was obtained by longitudinal burlap dragging. The dragging consisted of three passes: One immediately after normal finishing, the second 15 minutes after the first pass, the final pass 30 minutes after the second pass. The surfaces were cured under plastic sheets for four days and then further air cured at least sixty days before use.

TABLE I

PORTLAND CEMENT CONCRETE SURFACES

Aggregate Sieve Analyses

Screen Size	Crushed Limestone		Uncrushed Gravel	
	Wt.% Retained	Wt.% Passing	Wt. % Retained	Wt. % Passing
1"	0.0	100.0	0.0	100.0
3/4"	11.71	88.29	13.80	86.20
1/2"	24.61	63.68	20.55	65.65
3/8"	15.91	47.77	14.54	51.11
No.4	7.66	40.11	9.37	41.74
No.8	5.50	34.61	5.49	36.25
No.16	6.54	28.07	6.52	29.73
No.30	9.55	18.52	10.26	19.47
No.50	13.46	5.06	14.89	4.58
No.100	4.43	.63	3.89	.69
No.200	.34	.29	.48	.21
Pan	.29	--	.21	--

TABLE II

PORTLAND CEMENT CONCRETE

Compressive Strength

Core No.	Uncrushed Gravel Strength		Crushed Limestone Strength	
	Total (Lbs.)	Psi	Total (Lbs.)	Psi
1	66,600	2353	80,500	2845
2	80,000	2827	94,600	3343
3	84,100	2972	102,000	3604
Avg	76,900	2717	92,367	3264

3. Test Conditions and Procedures

The tires (B. F. Goodrich Silvertown Custom,* tubeless, 4-ply nylon cord, load range B, size E78-14) were preweighed, mounted, and balanced at the National Bureau of Standards. Pertinent conditions utilized in the test were:

Ambient Temperature in Tent	67-81°F(19-27°C) Average 75°F(24°C)
Wheel Load	1000 lbs. (454 kg)
Tire Pressure	30 psig (21×10^4 N/m^2)
Turntable Speed	50 rpm
Tire Speed	~25 MPH (~40 km/hr)
Wheel Lateral Frequency	7.4 strokes/min.

The traffic simulator was started on September 13, 1971, at 8:40 a.m. and was maintained continuously until 3:30 p.m., September 15th after 165,260 revolutions of the traffic simulator. At this time the simulator was stopped because the inside support bolts for one of the pavement boxes had sheared. All particulates were cleaned from the test facility and the pavement supports repaired. There was some additional sealing of the mylar tent around the test facility during the down-time.

The traffic simulator was restarted at 12:45 p.m. on September 16th and continued until 8:27 a.m., September 24th. 554,880 revolutions of the simulator were accumulated in this second run, for a total of 720,140 revolutions in the complete test program.

*The use of this brand of tire in carrying out this study shall not be construed as constituting an approval, endorsement, recommendation or disapproval of the product by the National Bureau of Standards.

This amounts to about 5,560 miles (about 8900 km). The summary of the traffic simulator operation is given in Table III.

During the test, gas analyses were made in order to monitor the possible buildup of volatile emission products. As the summary shows, several analyses were made early in the test. When these proved inconclusive, fewer volatile analyses were made.

After trafficking was completed the rubber particulates were cleaned from the tent, keeping the various areas of collection segregated.

C. SAMPLE COLLECTION AND ANALYSIS PROCEDURES

1. Particulate Collection Procedures

Three methods of particulate collection were used: (a) an Anderson* sampler, (b) a Hi-Vol sampler, and (c) vacuum and manual pickup from the traffic simulator.

(a) The Anderson sampler[6] was an eight-stage non-viable model. The Anderson sampler inlet was mounted on the side wall of the traffic simulator tent about 190 cm above the floor (about 115 cm above the pavement). Two sets of plates were used. The first set was turned on at 8:50 a.m., September 13, 1971, and turned off at 12:50 p.m., September 15, 1971, for a total of fifty-two hours collection time. The second Anderson run was started at 12:45 p.m., September 16, 1971, and turned off at 8:25 a.m., September 23, 1971, for a total of 163 2/3 hours collection time (Table IV).

*Certain commercial equipment is cited in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that this instrument is necessarily the best available for the purpose.

TABLE III

SUMMARY OF TRAFFIC SIMULATION OPERATION

Pre-Test

Time (Day:Hr:Min)	Event	Rotation Counter	Stroke* Counter
0:00:00	Simulator test, Hi-Vol #1	----	----
0:01:30	Volatile samples		
0:02:00	End of simulator test		
2:14:27	Hi-Vol #1 off		

Test

0:00:00	Simulator on	0	0
0:00:08	Volatile sample		
0:00:13	Hi-Vol #2 on Anderson #1 on		
0:03:53	Volatile sample		
0:05:58		18,501	2544
0:06:23	Volatile sample		
0:23:58		72,729	10,437
1:00:08	Volatile sample		
1:01:08	Hi-Vol change #2-3		
1:01:53	Volatile sample		
1:01:58	Brief stop of simulator		
1:06:38	Volatile sample		
1:07:38	Hi-Vol change #3-4		
1:23:58	Hi-Vol change #4-5	144,134	21,032
2:04:13	Anderson #1 removed		
2:06:59	Simulator off	165,260	24,151
2:07:18	Hi-Vol #5 off (Pavement section repaired)		

*The number of cycles on the change in length of the axle.

Time	Event	Rotation Counter	Stroke Counter
3:04:08	Resume test operation	165,260	24,151
	Hi-Vol #6 on		
	Anderson #2 on		
3:07:33	Volatile sample		
3:23:48	Hi-Vol change #6-7		
3:23:53	Volatile sample		
4:00:08		226,183	33,108
4:04:08	Volatile sample		
4:07:37	Hi-Vol change #7-8		
5:03:33	Hi-Vol change #8-9	308,535	45,435
6:07:13	Hi-Vol change #9-10	391,620	57,917
6:23:53	Hi-Vol change #10-11		
7:00:03	Volatile sample		
7:00:08		442,259	65,560
7:06:03	Volatile samples		
7:07:43	Hi-Vol change #11-12		
7:23:08		511,274	75,935
8:00:03	Hi-Vol change #12-13		
8:00:08	Volatile samples		
8:06:11	Volatile samples		
8:07:38	Hi-Vol change #13-14		
8:23:38	Hi-Vol change #14-15		
9:00:08		586,227	87,195
9:07:43	Hi-Vol change #15-16		
9:23:38	Hi-Vol change #16-17		
9:23:48	Anderson #2 off		
10:01:08	Simulator off	660,274	98,457
10:01:56	30.1 liters of monofluoro-dichloromethane added		
10:02:26	Leak sample #1		

Time	Event	Rotation Counter	Stroke Counter
10:02:56	Leak sample #2		
10:03:33	Leak sample #3		
10:04:17	Leak sample #4		
10:04:48	Leak sample #5		
10:05:44	Leak sample #6		
10:05:48	Leak sample #7		
10:07:48	Hi-Vol change #17-18		
10:23:39	Hi-Vol #18 off		
10:23:50	Simulator off	720,146	108,617
11:03:43	Leak test		
11:04:20	End of leak test #1		

TABLE IV

SUMMARY OF ANDERSON SAMPLER DATA

Plate	Set 1		Set 2		Size (μm) *
	(g)	(% total)	(g)	(% total)	
0	0.0053	61.3	0.0021	23.5	14
1	0.0011	12.7	0.00085	9.5	8.8
2	0.0009	10.4	0.0007	7.8	5.9
3	0.0009	10.4	0.00075	8.4	4.0
4	0.0003	3.5	0.0009	10.0	2.6
5	0.0001	1.2	0.0010	11.2	1.3
6	0.0000	0.0	0.0012	13.4	0.8
7	0.00005	0.6	0.00145	16.2	0.5
TOTAL	0.00865		0.00895		

*These sizes are the aerodynamic particle diameter which will have 95% collection on the stage indicated. They assume unity density, a 95% collection efficiency, and a spherical shape. The sizes are therefore only a guide as to the relative sizes actually collected.

(b) The Hi-Vol sampler was mounted on the side wall of the traffic simulator tent with its top 1.2 m above the floor 46 cm above the pavement). It was enclosed in a box and had a roof over it. The general design including the openings meet the EPA specifications[7] except the openings were only on three sides (Table V).

(c) The third method of particulate collection was by vacuum cleaner or by hand from the surfaces of the traffic simulator. The first collection was made at 10:30 a.m., September 14, 1971, when the simulator was briefly stopped to permit visual inspection of the tire tread and to collect a single particulate conglomerate from the floor adjacent to the tent entrance.

On September 16 (day 3 of the test), the entire traffic simulator was vacuumed before the pavement was repaired. On September 24 (day 11) the entire facility was again vacuumed.

After 55 hours of traffic simulator operation, 725.2 g were collected on September 16. After an additional 187 2/3 hours of traffic simulator operation, 1878.5 g were collected on September 24. The later weight includes a small amount of oil from a leak in the simulator hydraulic system.

TABLE V

Hi-Vol Filters

Filter	Mass (M) (g)	Sampling Time (T) Hrs:Mins.	M/T (mg/hr)
1	0.2430	62:27	*
2	0.5212	24:55	20.92
3	0.0618	6:30	10.30
4	0.0930	16:20	5.69
5	0.0618	7:20	8.83
6	0.0855	19:40	4.35
7	0.0330	7:49	4.22
8	0.0535	19:56	2.68
9	0.0650	27:40	2.35
10	0.0274	16:40	1.64
11	0.0174	7:50	2.22
12	0.0322	16:20	1.97
13	0.0180	7:35	2.37
14	0.0403	16:00	2.52
15	0.0177	8:05	2.19
16	0.0361	15:55	2.27
17	0.0139	8:10	1.70
18	0.0348	15:51	2.20

*Preliminary, M/T not meaningful

2. Volatile Collection and Analysis Procedures

The collection of samples of the gaseous effluent from tire wear consisted of pulling gas out of the tent through stainless steel tubing by means of an air pump. If the component to be analyzed was ozone, the gas from the air pump was pushed directly through the ozone analyzer system. If other types of gas analysis were to be conducted, the gas from the pump was collected in a gas sample bag and taken to the appropriate instruments.

The stainless steel tubing was 1/4 inch (6 mm) ID running from outside the tent to a location 91 cm inside the wall and 138 cm above the floor. The end of the tubing inside the tent was turned down to minimize the entry of particulates.

The gas sample bags were made of polyvinyl fluoride with quick-connect stainless steel fittings. Polyvinyl fluoride has been recommended for gas sample bags because of its impervious gas characteristics.[8] The bags held approximately six liters of gas when fully inflated.

The ozone content of the gas from the tent was determined by using the neutral buffered KI method that has been recommended by EPA.[9] The method was not totally calibrated, i.e., by putting a known concentration of ozone into the sampling tube. This technique was acceptable since the purpose of this measurement was to determine if the electrical machinery in the tent was generating ozone. No ozone was detected.

The gas chromatographic determination of C_1 to C_{12} hydrocarbons in gas bag samples was done by using the method of Papa, et al.[10] Minor modifications were made to the procedure and to the sampling system. Only stainless steel or tetrafluoroethylene parts contact the sample and all valves and lines are heated at 82°C to reduce condensation of higher boiling materials present in the sample.

The total hydrocarbons, carbon monoxide, and methane were determined using a Union Carbide Model 3020* air pollution analyzer. This analyzer is a gas chromatographic instrument using a flame ionization detector. The analyzer is fully automatic with provisions for self-calibration.

The determination of carbon dioxide was carried out using normal infrared absorption gas analysis. The gas sample is introduced into a 10 cm gas cell (stainless steel body) which is in turn attached to a gas handling system containing a U-tube mercury manometer to measure the pressure. A Perkin-Elmer Model 521* infrared spectrophotometer, with provisions for dry nitrogen flushing, was used to measure the intensity of the 4.25 μm abosrption band of carbon dioxide. A certified standard gas sample containing 330 ± 4 ppm carbon dioxide in nitrogen was used to calibrate the instrument. Calibration of the instrument was always done immediately before or after the gas samples were analyzed.

*Certain commercial equipment is cited in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that this instrument is necessarily the best available for the purpose.

TABLE VI

ANALYTICAL DATA

		Inside Tent						Other Locations				
Date	Time	Total HC (ppm)	CH_4 (ppm)	Total Less CH_4 (ppm)	CO (ppm)	CO_2 (ppm)	Ozone (ppm)	Total Hc (ppm)	CH_4 (ppm)	Total Less CH_4 (ppm)	CO (ppm)	Location
					Pre Trafficking							
9-10-71	10:15 a.m.	3.4	2.0 (1.7)(1)	1.4	3.8	-	<0.01	2.6	2.0	0.6	0.5	Outside Bldg.
					Initial Trafficking							
9-13-71	8:45 a.m.	4.6	3.5	1.1	3.4	430	-	-	-	-	-	
	12:30 p.m.	3.4	2.3	1.1	1.9	-	<0.01	-	-	-	-	
	3:00 p.m.	3.0	1.9	1.1	0.02	386	-	-	-	-	-	
9-14-71	8:45 a.m.	7.6	2.4	5.2	1.6	-	-	-	-	-	-	
	10:30 a.m.	-	-	-	-	-	-	7.4	2.0	5.4	1.5	Inside Bldg.
		-	-	-	-	-	-	3.2	2.0	1.2	1.6	Outside Bldg.
	3:15 p.m.	-	1.5(1)	-	-	-	-	-				
					Final Trafficking							
9-16-71	4:10 p.m.	4.6	2.0	2.6	0.7	-	-	-	-	-	-	
9-17-71	8:30 a.m.	4.3	2.0	2.3	0.8	-	-	4.2	2.0	2.2	0.8	Inside Bldg.
	12:45 p.m.	4.2	2.0	2.2	0.8	-	-	4.0	2.0	2.0	0.9	Inside Bldg.
9-20-71	8:40 p.m.	2.8	2.1	0.7	0.9	-	-	2.8	2.0	0.8	0.9	Inside Bldg.
	2:40 p.m.	3.1	2.0 (1.8)(1)	1.1	0.5	366	0.01	2.8	2.0	0.8	0.6	Inside Bldg.
9-21-71	8:45 a.m.	4.0	2.8	1.2	2.0	-	-	4.0	2.7	1.3	2.0	Inside Bldg.
	2:48 p.m.	3.6	2.0 (1.5)(1)	1.6	3.2	-	-	3.8	2.0	1.8	0.9	Inside Bldg.

(1) Analysis of methane by Gas Chromatography

3. Particulate Analysis

Mass Balance

The object of the tire wear study was to determine what happened to the rubber worn from tires during an accelerated wear test. All the solid material deposited in the tent, where the test took place, was collected and weighed; this weight was compared with the weight loss of the tires. There were some small losses of solid material which could not be collected from the air conditioning system of the tent.

Preliminary results, the weight of particulate matter collected and the lack of noticeable volatile emissions, indicated that most of the tire weight loss would be accounted for by the particulates. Thus an approximate mass balance was obtained. The mass balance, however, is complicated by the fact that the pavement also eroded and these products among other debris were collected with the tire wear products.

It could be easily seen in vacuum cleaner samples No. 1 and No. 4 that they contained a considerable amount of concrete, sand, etc. All other samples when viewed under a microscope showed lesser amounts of this material.

The object of the analytical work was to determine how much of each sample was tire tread. The referee ash method for fillers in rubber, ASTM Method D297 was used. In this method the samples are heated at

550°C until all the carbonaceous material is burned off, including all the tire rubber. However, tire tread usually contains several percent of fillers that will not burn away and which must be considered to obtain the quantity of tire tread in the sample. The residue thus consists of the tire fillers not burned off and the gravel and sand from the pavement. Thus, the weight of tire tread in the collected sample is calculated by the following method:

Percent tire tread = 100 - (% residue in sample) + (% residue in tire tread)

Weight of tire tread in sample = weight of sample x % tire tread.

Zinc oxide is present in tire tread as a filler. If the tread wears from the tires without any oxidation, volatilization, or other chemical change, then the percentage of zinc oxide in the tread portion of the collected samples should be the same as the percentage of zinc oxide in the original tire tread. However, if the rubber is changed, e.g., if it should undergo some volatilization, the ratio of zinc oxide to rubber should be different in the collected samples. Zinc oxide was determined by the method in ASTM D297. It was calculated as the percentage of zinc oxide in the tire tread present in the collected samples.

It is known that several samples were contaminated with oil from a small oil leak in the traffic simulator hydraulic system. It was thought that this oil could be

washed from the samples, removing this error. A number of solvents (petroleum ether, heptane, and trichloroethylene) were tried but it was found that materials besides oil were rapidly extracted from both the unused tire rubber and the samples. However, the amount of oil present is not believed to be large.

The biggest problem in the analysis is the inhomogenity of the samples, especially the vacuum cleaner samples containing large amounts of pavement. The nature of the samples is such that they cannot be homogenized. The presence of a small stone or pieces of pavement in the 1 to 2 gram analysis samples make for wide variations in the residue results. The results given in Table VII are for the total weight of the sample used. For some samples as many as five portions were burned.

The table shows that a total of 2201 grams of tire tread were collected. The tires lost 2298 grams. Therefore 4.3 percent was not collected. The uncertainty of this figure is rather large but it would appear that there have been losses of rubber in this test.

It is more difficult to draw any conclusions from the zinc oxide results. All but one of the collected samples shows a higher zinc oxide content than is present in the unused tire tread. This is what would be expected if some of the tire tread were volatilized or oxidized. However, in making a summation there is 3.5 percent more zinc oxide present in the collected material than in the tread lost from the tires. This implies

TABLE VII

*% residue in sample
-% residue in tire tread

RESULTS OF THE ANALYSIS OF THE TWELVE COLLECTED SAMPLES

SAMPLE	NET WEIGHT OF MATERIAL COLLECTED g	PERCENT RESIDUE	CORRECTED PERCENT RESIDUE*	PERCENT TIRE TREAD	WT. OF TIRE TREAD g	PERCENT ZnO
ATTACHED TO FENDERS						
Fender No.1 9-24	78.8	9.4	7.6	92.4	73	0.95
Fender No.2 9-24	166.0	6.8	5.0	95.0	158	0.97
Fender No.3 9-24	145.2	7.6	5.8	94.2	137	0.86
Fender No.4 9-24	192.6	6.8	5.0	95.0	183	0.98
Fell from fenders overnight 9-24	15.4	9.3	7.5	92.5	14	1.08
Miscellaneous 9-16	9.1					
Large from floor 9-16	140.7	12.1	10.3	89.7	134	1.02
Large from floor 9-24	435	9.9	8.1	91.9	400	1.00
Vacuum Cleaner Bags	560	39.9	38.1	61.9	347	0.89
No.1 - 9-16	684	13.3	11.5	88.5	605	0.81
No.2--Floor 9-24	114	9.4	7.6	92.4	105	0.88
No.4--Track & Interior Cover 9-24	64	31.9	30.1	69.9	45	1.07
TOTAL	2605				2201	
Unused Tire Rubber		1.75				0.85

Total Uncorrected Weight of Material collected 2605 g Weight loss of tires 2298 g
Corrected Weight of Tire Rubber Collected 2201 g

either analytical error or a spurious source of zinc. This may be an analytical problem caused by interferring materials present in the pavement. Pavement samples were analyzed and found to have negligible zinc. However, the pavement is inhomogeneous and there could be zinc or other interferring materials present as local inclusions. In any case the result makes the increase in the zinc oxide content of the collected rubber of doubtful significance.

Characterization of Collected Material

Two samples of the material collected during the test were processed in an attempt to identify or characterize the tire wear products. Sample #1 was obtained from the traffic simulator before the oil leak occurred; sample #2 after the oil leak occurred. These two samples were compared with sample #3, a butadiene-styrene rubber* and sample #4, a piece of tire tread cut from a tire used in this project.

Samples #1 and #2 were stirred in a blender with a saturated solution of sodium sulfate until the floating rubber particles had separated from the sand and gravel which settled to the bottom of the blender. The rubber was filtered, thoroughly rinsed with water, and air dried. The four samples were then dried over a three-day period under high vacuum at about 60°C. A one gram portion of each sample was placed in a 125 ml flask and extracted with three 100 ml portions of benzene. Each extraction covered a 48-hour period. The extracts from each sample were combined but were kept separate from the other samples. Loss of weight during the washing

*A vulcanized sample made by NBS according to ASTM D-15-72 Standard Formula 2B.

and extracting steps is shown in Table VIII. The extracted samples were again vacuum dried at about 60°C. Each was then pyrolyzed in a tube as shown in Figure 4.

The extracted and dried rubber sample was placed in the B section of the tube. The A section was then attached to a vacuum line and evacuated over a 24-hour period to 0.1μm and sealed. Pyrolysis was affected by placing part B of the tube, containing the rubber sample, in an electrically heated furnace and maintaining a temperature of 450°C for two hours. During the pyrolysis part C of the tube was cooled to -196°C by immersing it in a dewar flask filled with liquid nitrogen. After pyrolysis the tube was again attached to a vacuum line through the standard tapered joint E. The break seal D was broken in the standard fashion and all of the volatile materials distilled into a small tube.

The procedure described in the proceeding paragraph was carried out with each of the four samples. Material from each of the four small tubes was injected into a very sensitive vapor phase chromatograph. The recorder traces for the four samples were virtually identical. Each trace showed a peak at the known retention time of styrene but nothing that specifically indicated butadiene. The multiplicity of compounds in the pyrolysate mixture suggested a very complex pyrolysis mechanism. Isolating and identifying each of the compounds produced by the pyrolysis was not justified for this effort.

TABLE VIII

SAMPLE	ORIGINAL SAMPLE (g)	AFTER WASHING (g)	BEFORE EXTRACTION* (g)	AFTER EXTRACTION (g)	SOLUBLE FRACTION
#1	3.9920	2.1200	0.9985	0.7355	.266
#2	5.31	4.11	0.9995	0.7165	.283
#3			0.9670	0.7505	.224
#4			0.9986	0.7735	.225

* ~ 1 g aliquot

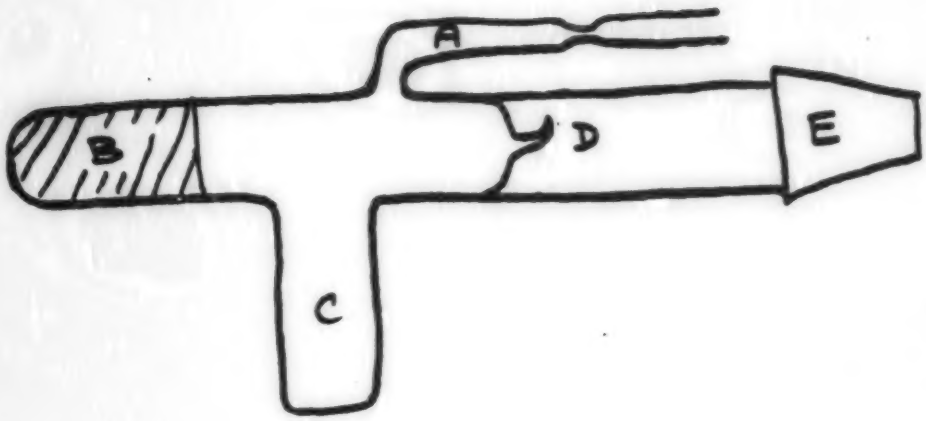


FIGURE 4

The non-volatile oils remaining in the pyrolysis tubes after removal of the volatiles were smeared on salt crystals and studied in the infrared spectrograph. These studies suggested only that the oils were aliphatic hydrocarbons. The material left in the B section of the pyrolysis tube, the part that had remained at an advanced temperature for two hours, was found to be largely carbon with small amounts of metallic substances.

Other attempts at infrared analysis were equally fruitless. The samples were looked at by ATR (attenuated total reflectance infrared spectroscopy) but no structure could be seen other than a hint of a C-H line. Direct transmisaion measurements were equally uninformative. Apparently the presence of carbon black in the tire blocked any structural information. The study of various tubber samples suggested that rubber shredded from tires during tire wear studies, the rubber in the original tire, and rubber which has not been fabricated into tires are largely of the same chemical composition. If the particles shredded from the tire are large enough to be visible then the volume of original rubber present is too large to permit the detection of chemical reactions which have taken place only on the surface. Although it is known that free radicals are produced when rubber is mechanically abraded or cut, in the case of tire rubber, the presence of large amounts of carbon prevent the use of electron spin resonance, infrared studies, or any common radical detection techniques.

4. Tent Leakage Tests

Because the tent gas hydrocarbon analyses seemed to follow the outside air analyses very closely it was

decided to run a leakage test to estimate the loss rate of gas from the tent. A refrigerant gas (monofluorodichloromethane) was injected as a tracer through the tubing normally used for sampling the tent atmosphere (Table IX). Subsequently, samples of the tent atmosphere were withdrawn at frequent intervals and the decrease in concentration of the tracer gas was followed using infrared spectroscopy. The first leakage test was run during the last full day of operation of the traffic simulator (September 23, 1971). Results of this first test indicated a high leakage rate. However, there was the possibility that some of the tracer gas had condensed on the air conditioner cooling coils.

A second leakage test was run utilizing two different gases as tracers, monofluordichloromethane and propane, and with the air conditioner compressor shutdown. The second test was run on September 28, 1971, with the tent temperature at 33°C and the room at 34°C. The tires and rims had been removed from the traffic simulator and one of the original three filters had been replaced before the tent was resealed for the test. Air circulation typical of that for the tire tests was simulated by revolving the traffic simulator at normal speed and by operating the air conditioner blower.

All leak tests indicated a half life for the tracer concentrations of approximately 30 minutes.

D. RESULTS AND CONCLUSIONS

1. Particulate

The main results are treated below as items.

(a) Mass Balance - Using Zn (determined as zinc oxide) as a tracer we can account for nearly all of the weight loss from the tires.

TABLE IX

LEAKAGE TEST DATA

1st Test (9/23/71)

Time, Hours		Tent Gas Analyses Optical Density at 8.98 μm
10:32 to 10:33	Introduction of monofluorodichloromethane (30.1 Liters at 94°F, 756 torr)	
11:03		0.310
11:33		0.131
12:10		0.049
12:54		0.026
13:25		0.020
14:21	(top of tent)	0.018
14:25	(bottom of tent)	0.018
	Approximate logarithmic decay time	30 minutes

2nd Test (9/28/71)

Time, Hours		Tent Gas Analyses Monofluorodichloromethane Optical Density at 8.98 μm	Propane Optical Density at 3.42 μm
8:31 to 8:33	Introduction of monofluorodichloromethane (30.0 Liters at 94°F, 760 torr)		
8:34 to 8:35	Introduction of Propane (10.0 Liters at 94°F, 760 torr)		
8:50		0.446	0.024
9:08		0.263	0.014
9:35		0.087	0.005
11:05		0.017	0.002
11:45		<0.002	<0.002
	Approximate half life	28 min.	33 min.

Conditions:

One meter infrared gas cell, 733 torr pressure for each run, Perkin Elmer 521 Infrared Spectrophotometer.

There were five tires available for the test. Four were used on the simulator while the fifth was available in case of a tire failure. Prior to weighing, the tires were stabilized in a warm room (-38°C).

Weight Lost from Tires

Tire	Change in Weight (g)
#1	-628.5
#2	-484.5
#3	.8
#4	-6 [illegible].6
TOTAL WEAR LOSS	-2298.4
#5 (not used)	-1.4

It is estimated that these weights are good to about ± 1.5 g for each tire. The unused tire had a loss of 1.4 grams which is probably due to uncertainty in the weighing process.

Analysis of the material collected accounted for 2201 grams of rubber (by subtracting the mass of pavement from the total matter collected) leaving 97 g or less than 5% unaccounted. This amount of material could easily have been missed by the collection procedures. For instance it was not practical to clean the air conditioning system and filters and it is known that some material was deposited there.

It is interesting that the Hi-Vol sampler collected only a negligible amount of particulate matter. It must be stressed, however, that the test conditions were very dissimilar to normal wear and we are specifically not making any extrapolation of this data to typical driving conditions.

The conclusion is that within the accuracy of the experiment the weight loss of the tires is accounted for by the particulate matter.

(b) Size Distribution - The Anderson impactor results (Table IV) appear to indicate a change in the distribution of sizes as the test progressed. There seem to be more small particles later (Set 2). This may be due to the tires and the pavement becoming run-in as asperities on the pavement are worn down, etc. However, from a comparison of the weight collected by the Anderson and the Hi-Vol compared to the total weight of particulates collected (1.2 g versus 2606 g) it appears that very little material was of a size to remain airborne long.

This is corroborated by the way the wear products appeared. Much material was apparently thrown up against the inside of the fenders where it agglomerated and hung for a while before being dislodged and thrown to the horizontal surfaces in the traffic simulator. Some of these agglomerates were as large as 1 cc.

The conclusion is that in this experiment very few of the tire wear products are in the size range of suspended particulates.

(c) Chemistry - The particulate matter collected seemed to be mostly rubber. There was undoubtedly some oxidation of the wear products and probably a great deal of scission in the elastic chains of the rubber. However, we could detect no chemical changes.

2. Volatiles

The gas samples taken during the test runs show no evidence of volatile wear products formed during the test. In other words, the hydrocarbon and CO content

of the samples was essentially the same as that of the ambient air outside the test tent, as can be seen in Table VI. The composition of the ambient air itself was quite variable--a factor which did not help the determination.

If all the 97 grams of tire weight loss not yet accounted for went into volatile hydrocarbons this might be seen above the background. A very rough calculation shows this might cause a 1 ppm rise in hydrocarbon concentration.* Such a change in the hydrocarbon concentration was not noticed. Our data show the hydrocarbon concentration inside the tent was the same as that outside to within 0.3 ppm.

This project measured tire wear under severe cornering conditions and found little airborne particulates (by weight). While it is believed that most tire wear occurs in cornering conditions, the relative amount of airborne particulates for our test conditions, for normal cornering conditions, and for straight driving conditions is not known. It will be necessary to assess the amount of airborne particulates under more representative driving conditions to know the significance of tire emissions to air pollution.

The conclusion is that in this experiment very little of the tire wear products could have been volatiles. There is no conclusion as to their identity.

*Assume: (i) 97 grams worn off evenly over 243 hours; (ii) gas half-life of 30 minutes; (iii) tent volume a 3.5 m radius hemisphere (~90 m^3); (iv) steady state; (v) hydrocarbon average molecular weight of 50.

3. Application to Road Conditions

The tire tread wear pattern was very uneven. After the test it could be seen that at least some wear occurred as rubber was rubbed or feathered off the edges of the tread segments. Presumably this was due to the constant-cornering mode of the test. In other respects the test was realistic and probably approximates some road conditions.

If one could establish that most tire wear occurs in just such maneuvers as cornering and that very little wear occurs on straight driving, then one could perhaps conclude tentatively that this test has some application to the emissions expected in real road tire wear. In fact it is believed that most wear does occur in cornering maneuvers. The problem is that we have no idea about the relative amounts of very fine particles in straight driving vs. cornering. Since the fine particles are more likely to cause air pollution, this is very important.

E. COMMENTS AND SUGGESTIONS

This study has not been as conclusive as was desired. The apparent high volatile leak rate from the tent enclosure was not expected and is somewhat difficult to understand. Another problem with our procedure is the wear rate which is higher and different from what would be found in normal road operation. There are several possible methods which could be used for future studies.

A future study could be similar to the one covered by the report except that the enclosure should be much better sealed. A possible test facility could be setup in a space simulation chamber. This would permit a controlled atmosphere to be used as well as the knowledge that the only volatile losses would be from condensation on the walls.

A second variation would be to use a vertical donut-shaped track with the tires running around the inside. With appropriate controls for the tires, this would permit simulation of straight driving or any degree of cornering. The use of a reduced size tire would facilitate the study.

Another possible method would be to use a steel test wheel covered with a mesh-reinforced gravel and epoxy pavement. Although the tire contact area would not be of a normal road shape, the wear surface would be similar to that of a normal road.

Another possible method would be to mount collection horns immediately behind the tires on a test vehicle. It would be necessary to collect background samples also.

The Cornell Aeronautical Laboratory[11] has tested a scale model road simulator which can be used to study tire wear emissions. The basic principle is to use an air bearing to support a belt under the tire. Although the facility will not provide a normal road surface, it will provide a flat pavement and also provide adjustments for simulation of cornering, etc.

The availability of on-line analysis facilities is also important since the rubber and its decomposition products are subject to oxidation. (Our particulate samples had to be shipped from Indiana to Washington, D. C. for analysis.)

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